Notebook, N-06-10-05

This notebook was used during October 1906. All entries are by Edison. Included are notes regarding the treatment of nickel-cobalt ores that contain arsenic, along with entries relating to the preparation of the metals for use in storage batteries. The pages are unnumbered. Approximately 20 pages have been used.

Oct 5th 1906.

Working Cobalt Arsenides + Wad

Realgar dissolves in Sol KOH.

Why not ignite roasted Co arsenide with S in excess + dissolve out realgar, or volatilize by heat,

Carb Soda to which sulphur is added mixed with Arsenide fuse, the Cobalt remains as Sulphide free of Arsenic Watts Dic — possibly charcoal should be added.

Roast + reduce to Speiss, put in boiling H_2SO_4 oxdze As to As_2O_3 which volatilizes leaving CoS or CoO.

Pass SO_2 Hot over powdered speiss. Realgar formed, ∴ S to Co 175 HU As_2O_3 1547 HU SO_2 710 HU.

Roast speiss to As_2O_3 pass CS hot, forms CO + COS or CoO,

Relative affinity of Sulphur for metals

Strongest
Palladium
Mercury
Silver
Copper
Bismuth
Cadmium
Antimony
Tin
Lead
Zinc
Nickel
Cobalt
Iron
Arsenic
Thallium
Manganese
Weakest

Try Speiss roasted in arc furnace, magnesium lining -

Try Speiss anode in in KS. also KS polysulf use Ni Cathode CoS + Realgar forms at anode, realgar dissolves in KS, possibly As also deposit at Cathode use Cloth bags -
Mud roasted & smelted to an anode & operations repeated till pure,

To separate Co from Ni ignite the oxides, dissolve out CoO by dilute H_2SO_4 in which NiO is practically insoluble -

Another way reduce oxides to metal dissolve out Cobalt by Cupric Sulphate - The Copper & Nickel left is melted to an anode & Copper plated out in acid solution -

Another way reduce to metal
& form anode | Mercury Cathode,
when Cathode loaded with Co Ni
to battery consistency - put in
shallow dishes & allow Co to self
oxidize & collect as formed metal
nearly all oxidized when Ni will
commence to oxidize -
Then Either allow Ni to oxidize or
distill off Hg in Vacuo & get
metal Ni -

Arsenious acid is reduced to metallic
arsenic in slightly acid solutions
by metallic Zinc. requires 1½ times
weight of arsenic according to Downs.
If the As is in form of arsenic acid
it throws down ferric arsenate instead
of metal,

Cheap Hydrogen Sulphide

Steam + SO_2 passed through furnace filled with red hot coke. SO_2 reduced to S by Carbon water forms H + CO the H + S combine. Coke is kept red hot by blowing air in intermittently as in making Water gas.

Also Producer gas from soft Coal passed over red hot pyrites, by action of S + Hydrocarbons HS generated.

Another Scheme action of CO_2 on Na Sulphide,

Hoffner says Arsenic in Cupric Chloride Solution is thrown down by Caustic Lime or Cu Oxide,

Impure Electrolytes purified thus -

Newark
Sulphates Cu Ni Zn Crystalized The Arsenious acid & H_2SO_4 are yielded on boiling mother liquor

Chicago
Bluestone crystalized out, mother liquor Evaporated This gives a mixture of Bluestone & arsenious acid, by using a minimum amount of water The blue stone dissolves leaving the As_2O_3

Perth Amboy
$CuSO_4$ Crystalized out - Mother liquor treated with Iron, Copper thrown down Then stopped The Mother liquor Contains Cu + 60% As_2O_3 sold for Ash green coloring matter.

Mansfield Germany
Arsenic deposited out of Co Ni Sulfates by Cathodes with density of 30 milamp per inch, The Sulfates of Co Ni are then crystalized out, any Copper in solution is deposited with the As as a sponge mass Cu then dissolved out by weak acid

Oxalic acid precipitates Co Ni Fe
from Sulphate Solution by adding an
excess of Arsenious ore

Arsenious A sol hot Oxalic
Separates out on Cooling -

As_2O_3 Easily Sol in Arsenite Ammonia
hot, 7 to 150 cent. Separates out on Cooling -

As_2O_3 Sol hot Oxalate Potash

Dilute SO_4 at 80 dissolves about
1¼ pts of As_2O_3 to 100 of Solution
at 185 deg Cent about ½ part to 100

100 pts boiling Water dissolve
about 10 parts As_2O_3 in 3 hours

Pass H_2S through heated roasted arsenides + Reduces the Co Ni to metal + Volatilizes the Realgar

Pass SO_2 thro arsenides unroasted + Volatilizes the Realgar - + oxidize the Co Ni. Then remove + put in Tower with 6 Q of times bulk of Quantity + pass H or Co reduce to metal then lead out Cobalt by Cupric Sulphate, when all out Continue treatment with air + Cupric Sulphate to reduce the Copper - Then Wash out the metallic Nickel

Roast ore dead until ~~all~~ a test sample all dissolves (14) all Co Ni - Then 1st Batch treat to saturation with dilute H_2SO_4 = Wash out + again treat with 1/2 or 1/4 portion till all Co Ni dis use this liquor on Batch No 2

wash out when saturated with Co Ni - & add fresh ~~[illegible]~~ Lot H_2SO_4 until all metal dissolved & liquor is saturated. Then add 1/2 or 1/4 portion of H_2SO_4 & dis all Co & Ni & add the liquor to Batch No 3. & so on - after several Batches have been worked

The Liquor from the several Batches crystalizes when they have crystalized out as far as practicable. Take the Mother liquor & evap down for a further Crop of Crystals & finally add this mother liquor to a fresh batch of ore & saturate ~~the acids with Co Ni & if~~ crystalize out the Co Ni & that evap the mother liquor to dryness & mix with Crude ore & roast to drive off the arsenic -

Redissolve all the Crystals & Crystalize 2nd time slowly
Dry Crystals in Centrifugal
Wash them with a little
Cold Wash Water —
Boil this wash water
down & put it in the
Leaching Solutions used
on fresh ore —

The pure Crystals are dissolved
in Water & Bi Cu^T first precip
by H_2S, filter & then throw
down Arsenic, boil & filter
~~add Co Hydroxide &~~
~~pr~~ ~~Co~~ ~~boil~~ to
~~Sol~~ ~~Ferric~~
Oxidize with Nitric, Hypo or
Chlorine, & add Ni Hydrox or
$Co(OH)_2$ to boil out Ferric —
After that what's —

Possibly add $Ni(OH)_2$ & boil
after Co is peroxided &
throw down all the Cobalt

or Evaporate the Sulphate to
dryness then roast in
furnace & distill off &
saved what acid can &
Reduce the mixed oxides
to metal & separate the
Co by Cupric Sulphate &
air, afterwards removing
the Copper by Cementing
the treatment. The Nickel
will remain metal &
Can be used at S Lake
The Co Sulfate is roasted
& reduced to metal &
fused to anodes,

Or what is ably better Seperate
the Nickel by crystalizing out
as Double Sulphate Ni+K
in hot solution -

Ignite the $CoSO_4$ + $KNiSO_4$
seperately - save H_2SO_4 from both
Salts & get oxides. The K from
the $NiSO_4$ K leached out
Reduce to metals

Sulphides of As more volatile than metal itself

H reduces arsenate lime to As metal which volatilizes

As volatilizes at dull red. visible in the dark

Arsenious acid which crystallizes from hot solution is a As_2O_3 white sublimed As_2O_3 is BAS_2O_3

Very finely divided As when moist or dry is pyrophoric

H dont act on Arsenic

As heated below red in KOH. forms arsenite K- + arsenide of K + liberates H.

With boiling H_2SO_4 arsenic forms As_2O_3 + liberates SO_2

With dilute Nitric forms As_2O_3 + liberates Nitric Oxide

Sb oxide is dissolved out of As_2O_3 by HCl if done carefully only little As_2O_3 is left out - CoPS HCl

Process

As_2O_3 when sublimed should it contain any Sulphuretted acid KOH & resublime —

A Boiling Solution of KOH when saturated with As_2O_3 + then cooled deposits the As_2O_3 Should be able to remove As_2O_3 from the ore this way —

As_2O_3 Solidifies at 218 Cent,

As_2O_3 in aqueous sol. Iron precipitates the As as Ferric Arsenite If HCl present the most of the arsenic escapes as Asthydrogen.

As_2O_3 heated with Lime resolved into arsenate of Lime. + sublimed Arsenic metal, Similar reaction takes place with Carb K, -

1 pt As_2O_3 dissolves in 7.72 pts 60° Fahr water – others say 1 to 12 with As_2O_3 in excess.

Arsenite of silver on heating gives off As_2O_3 + leaves a mix of Arsenate of Ag + metallic Ag

Arsenite of lead alone withstands a red heat without decomposition. + Arsenite of Hg is but imperfectly decomposed

Arsenic acid dis in 6 pts cold & 2 pts hot water.

Arsenate Ag dont dis in NH4 salts

AsH_3 = Arsenuretted H.
Gehlen + Bullnecke Killed 6 by accidentally inhaling it – has a most repulsive smell
Burns in air at yellow heat. Self burns like a gas + forms H_2O + As_2O_3
$CuSO_4$ absorbs all of the gas leaver pure H. Condensed in very slow. Yields

Tri-arsenide Cont

Realgar heated out control with air
volatilizes much below red heat,

Realgar burns in air to As_2O_3 &
SO_2 –
Heated with H_2SO_4 forms As_2O_3
& SO_2 –

As_2O_5 or As_2O_3 is never completely
precipitated from solution by H_2S. or
Alkaline hydrosulphides.
Can be mostly eliminated by
1st filtering liquid in a closed vessel
after saturation with H_2S, heat warm
gently several days –
2nd saturating it anew from time to time
because if not saturated the acid liquid
redissolves one part of the arsenic from
the arsenic sulphide.
3rd filtering the liquid from the precip
before driving off the excess of H_2S.

Trichloride Arsenic boils 132 Cent, Evaporates in air and temp, fumes, highly poisonous. –

Fluoride of Arsenic very volatile, boils 63 Cent. If evap in air As_2O_3 left behind,

As_2O_3 very soluble Ammonia when heated, in cooling almost wholly deposited as crystals As_2O_3 as about any NH4 (Basic salt above)

Acid Salt. Viscid mass settles bottom of liquid, agitation & warmth it dissolves. If the acid & salts crystallize out.

As_2O_3 dissolves easily in KOH, only slowly decomposes K_2CO_3 when heated,

As_2O_3 in excess dissolved in KOH. Cold. Only alkaline liquid formed. which dont crystallize

Process

Process

Sodium Arsenite, viscid yellow
Can be Conc to syrup — if has
excess Arsi, acid salt cant
be crystallized.

Magnesia absorbs the vapors
of arsenious acid passing
over it, without liberating As.
the compound only evolves
As when very strongly ignited.